KIRK-OTHMER

CONCISE ENCYCLOPEDIA OF CHEMICAL TECHNOLOGY

A WILEY-INTERSCIENCE PUBLICATION
John Wiley & Sons
NEW YORK · CHICHESTER · BRISBANE · TORONTO · SINGAPORE

Library of Congress Cataloging in Publication Data:

Main entry under title:

Kirk-Othmer Concise encyclopedia of chemical technology.

"A Wiley-Interscience publication."

Abridged version of the 24 volume Encyclopedia of chemical technology. 3rd ed. New York: Wiley, c1978–c1984.

Includes index.

Executive editor, Martin Grayson; associate editor, David Eckroth.

1. Chemistry, Technical—Dictionaries. I. Kirk, Raymond E. (Raymond Eller), 1890–1957. II. Othmer, Donald F. (Donald Frederick), 1904– . III. Grayson, Martin. IV. Eckroth, David. V. Encyclopedia of chemical technology. VI. Title: Concise encyclopedia of chemical technology.

TP9.K54 1985 660'.03'21 84-22006

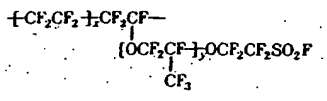
ISBN 0-471-86977-5

ISBN 0-471-51700-3 (pbk.)

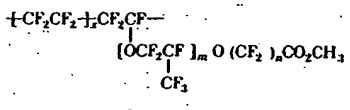
Printed in the United States of America

10 9 8 7 6 5 4 3 2

new electrolytic process for chlor-alkali production using perfluorinated ion-exchange membranes (see Alkali and chlorine products). Flemion is a carboxylic acid type. The different ion-exchange groups greatly affect membrane properties.



Nafion polymer



($m = 0$ or 1, $n = 1$–5)
Flemion polymer

Both polymers are melt-processable and can be fabricated into films by extrusion-molding. These films can be easily converted to the corresponding ion-exchange membrane by alkaline hydrolysis.

Preparation

The general procedure includes synthesis of a perfluorovinyl ether moiety with a functional group, its copolymerization with tetrafluoroethylene in the presence of a radical initiator in an aqueous or inert organic medium, and the formation of a membrane.

Fabrication. The crystallinity of the copolymer depends upon the content of the functional conomonomer. Amorphous or partly crystalline copolymers are fabricated into films (100–250 μm thick) with conventional extrusion techniques. The films are usually reinforced with Teflon cloth and converted to sulfonic- or carboxylic-acid-type ion-exchange membranes by alkaline hydrolysis.

A sulfonic acid group can be converted to a carboxylic acid group:

$$\cdots -O(CF_2)_nSO_2X \rightarrow\rightarrow \cdots -O(CF_2)_{n-1}CO_2H$$

(X = Cl or F)

The sulfonyl halide group is converted to sulfinic acid by reduction and then the carboxylic acid group, having one CF_2 less than the original chain of sulfonic acid, is formed through a desulfonylation reaction.

Applications

In the electrolysis of brine, a cation-exchange membrane is used. DuPont has developed a variety of Nafion series. The Nafion 300 series produces 10–20% caustic soda. For the production of 20–28% caustic soda, the Nafion 200 series was developed. The Nafion 900 series membranes are carboxylate–sulfonate two-layer membranes with ca 95% current efficiency at 33% caustic soda.

Asahi Glass has developed the Flemion series. For the production of 30% caustic soda, a standard Flemion 230 is used advantageously with a current efficiency of 94%. With the Flemion 700 series, gas bubbles can be removed easily from the membrane surfaces.

A new electrolytic process with a zero-gap cell, called the AZEC system, combined with Flemion 723 or 753 and a new electrode system, has resulted in drastic reductions in energy consumption.

Asahi Chemical Tokuyama Soda improved the electrolytic performance of Nafion-type membranes by chemical modification of the cathode-side surface of the carboxylic acid-type membrane.

MASAAKI YAMABE
Asahi Glass Company, Ltd.

Eisenberg and H.L. Yeager, eds., *Perfluorinated Ionomer Membranes*, *S Symposium Series 180*, American Chemical Society, Washington, D.C., 2.

Ukihashi, *Chemtech*, 118 (Feb. 1980).

Nagamura, H. Ukihashi, and O. Shiragami, *paper presented at the Symium on Electrochemical Membrane Technology in 1982 AIChE Winter eting*, Orlando, Fla., 1982.

PERFLUORO COMPOUNDS. See Fluorine compounds, organic.

PERFUMES

Perfumery is the art of producing fragrances through the combination of odoriferous substances. The word perfume is derived from the Latin meaning "through smoke". Throughout history, perfumes have played an important role in human lives, and have been associated with notions of happiness, beauty, and satisfaction. Until this century, fragrance materials have been derived from natural sources, which has placed limitations on odor types and markets (see also Cosmetics; Odor modification). The increased use of perfumes in the last thirty years would have been impossible without the development of the chemistry that allowed the invention of totally new odoriferous molecules as well as the synthesis of natural ones. Fragrances are no longer a luxury for the rich but today are incorporated routinely in a great number of products that are in daily use.

Fragrance Raw Materials

Natural products. Essential oils are volatile materials produced from odorous plant material, generally by water or steam distillation or by expressing (see Oils, essential).

A concrete is an extraction almost exclusively from vegetable origin such as leaves, bark, flowers, and fruit. This is normally obtained by extraction with hydrocarbon solvents.

Absolutes are the alcohol-soluble portion of concretes, obtained by extracting the concretes with alcohol. Resinoids are perfume materials obtained by extraction of plant resinous substances with hydrocarbon solvents.

Tinctures are alcoholic solutions. In perfumery, these are generally the solutions obtained by maceration of various odorous materials with alcohol.

Natural products used in perfume include ambergris, benzoin, castoreum, civet, clove leaf oil, galbanum, jasmine absolute, labdanum, maté, melilot, mimosa, musk tonquin, myrrh, oakmoss or mousse de chêne, olibanum, opopanax, orris, patchouli, rosemary oil, sandalwood oil, vetivert oil, and violet leaves absolute.

Aroma Chemicals

During the last 20 years, there has been a rapid advance in the capabilities of instrumental techniques for the separation and identification of volatile organic substances. Of particular importance to the perfumery industry was the development of capillary gas chromatography columns and the ability to use them directly in tandem with a mass spectrometer. Computer technology is used to interpret the vast amount of data generated by such a combination of instruments. These developments along with Fourier transform nmr spectroscopy have allowed discovery and identification of extremely minute odoriferous samples and have revolutionized not only the analysis of essential oils and extractives but also the direction of the synthesis of aroma chemicals.

Research in aroma chemicals can be divided into three general categories: (*1*) duplication of naturally occurring chemicals, for example, phenethyl alcohol, which occurs in rose oil; (*2*) chemical modification of abundant, naturally occurring materials, eg, acetylated vetivert oil ("vetivert acetate") from vetivert oil, and vanillin (qv) from lignin (qv); and (*3*) synthesis based on industrial organic feedstocks, eg, nitro musks.

Aroma chemicals are usually cheap and available in any needed quantity (see also Alcohols, higher aliphatic; Aldehydes; Benzaldehyde; Benzoic acid; Cinnamic acid; Cinnamaldehyde; Cinnamyl alcohol; Coumarin; Esters, organic; Indole; Ketones; Salicyclic acid and related compounds; Terpenoids; Vanillin).

Odor Vocabulary

The descriptions and groups of fragrance raw materials are helpful in evaluating existing aroma chemicals or newly developed materials. To illustrate the use of the odor vocabulary, two well-known materials are